The Dow Chemical Company

Using Catalysts to Directly Oxidize Propylene to Propylene Oxide

Propylene oxide (PO), a gaseous petrochemical, is a key ingredient in polyurethane foams, coatings, sealants, and adhesives used by the housing and automotive industries. The value of products manufactured using PO derivatives was estimated at $10 billion in 1995 (1.5 million metric tons), but existing PO production methods were slow and costly. The Dow Chemical Company (Dow) developed a plan to use silver or similar catalysts to directly oxidize propylene to propylene oxide. Catalysts accelerate the transformation of one chemical to a useful new chemical. Dow's proposed production method would be faster, cheaper, and more environmentally friendly. Because direct oxidation is hard to control, the company was unable to raise sufficient internal funds for comprehensive research and development of this high-risk process. The oxidation must produce only PO in order to succeed. Dow applied to the Advanced Technology Program (ATP) for support, and ATP awarded funding for three years as part of a focused program, "Catalysis & Biocatalysis Technologies." Researchers from the University of Michigan, Washington University, and Texas A&M University collaborated with Dow to support this project, which began in 1995.

In addition, as a member of the beamline user facility located at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory, Dow was able to do leading edge materials characterization as part of the ATP project to improve their understanding of how to control oxidative catalysis. The use of this facility to advance in situ catalyst characterization using soft X-ray detection technology [Near Edge X-ray Absorption Fine Structure (NEXAFS)] led to more industrial users exploring the potential of this in situ tool for catalyst characterization long after the ATP award.

Dow project researchers developed a new PO process that reacted propylene with oxygen in the presence of hydrogen. However, due to volatility in the price of hydrogen, the direct-oxidation process developed by Dow researchers is not yet cost-competitive. They did succeed in developing X-ray methods to observe chemical reaction intermediates with silver, gold, and other catalysts. They also developed a new family of oxidation catalysts. This work contributes to a better understanding of oxidative catalysis, enabling a new methodology for testing catalysts. They received six patents for their new methods and catalysts, and they disseminated their knowledge through numerous publications and presentations. Dow and other companies continued to use similar partial oxidation techniques at the NSLS facility to characterize the structure versus function relationships of new catalysts, and to more efficiently produce other industrially important chemicals for use in polymers, metal-polymer interfaces, and lubricants. As of 2004, the research on the new PO process was ongoing at Dow. The global PO market volume grew to 5.1 million metric tons in 2003 ($238 billion) and is expected to reach 6.3 million metric tons by 2007 ($294 billion).

COMPOSITE PERFORMANCE SCORE

(based on a four star rating)

* * *

Research and data for Status Report 95-05-0002 were collected during April – May 2004.

Propylene Oxide Is a Versatile and Practical Chemical

Propylene, a simple substance with three carbon atoms, is a flammable gas obtained by cracking petroleum molecules. One of the products formed when propylene is gently reacted with oxygen is propylene oxide (PO), a volatile, colorless gas with an ether-like odor. PO has many applications: 60 percent of the manufactured PO is used to make polyurethane foams (for upholstery), coatings, sealants, and adhesives, primarily in the automotive and housing industries; 20 percent of the PO is used to make propylene glycol, a component in fiberglass-reinforced plastics, foods, cosmetics, pharmaceuticals, airplane de-icing compounds, and hydraulic fluids; and the balance is used to produce lubricants, surfactants (detergents), and flame retardants.

Global consumption of PO had reached 1.5 million metric tons annually in the mid 1990s. Historically, consumption had been steadily growing at 6.2 percent annually, which meant that manufacturers had to increase production capacity or look for ways to produce PO more efficiently to meet demand. In a 1.5-million-metric-ton industry, a 6.2 percent annual growth rate meant increasing annual PO production by nearly 100,000 metric tons.

Current Production Is Inefficient and Energy-Intensive

In 1995, traditional processes for making PO were energy-intensive and inefficient. The processes used many pieces of equipment, involved multiple steps, and created large quantities of by-products and waste, which increased the cost of production as well as the impact on the environment. The primary production method used in the United States, called the chlorohydrin process, involved combining propylene and chlorine in a chemical reaction with water to produce an intermediate product called propylene chlorohydrin, which was then processed with caustic (sodium hydroxide) or with lime (calcium hydroxide). The output from this process includes several products: a dilute brine (sodium chloride in water) or calcium chloride, PO and propylene glycol. The resulting PO requires distillation for further purification before it can be used. Because the wastewater dilute brine produced is about 40 times the volume of the PO, using the chlorohydrin process results in disposal problems.

The hydroperoxide process is another costly method for producing PO. This process uses ethylbenzene with oxygen to produce an organic-hydroperoxide. The hydroperoxide is used to oxidize propylene to PO, which is then purified. This process results in a large quantity of by-product, phenylmethylcarbinol, which is dehydrated to styrene, another useful chemical. Although this process has a high conversion rate (approximately 90 percent), the ratio of styrene to PO produced is approximately 2:1 (that is, 640,000 metric tons of styrene result from 285,000 metric tons of PO produced annually). Thus, the hydroperoxide manufacturing process depends on a strong market demand for both PO and styrene.

Researchers at various companies had succeeded in directly oxidizing a petrochemical similar to propylene, called ethylene. Beginning in 1937, researchers showed that ethylene could be directly oxidized to ethylene oxide (EO), a chemical similar to PO, using silver catalysts in a process that reduced raw material consumption and energy waste. Researchers had steadily improved EO production efficiency by using additives to the silver catalysts. This success stimulated the search for an analogous direct oxidation process for PO. However, because propylene is more combustible than ethylene, the catalysts used in EO production did not work for PO. Researchers had made attempts in the 1970s and 1980s, but these failed due to the lack of conversion efficiency and low selectivity to PO.

Direct Oxidation Would Cost Less and Minimize By-Products

Researchers at The Dow Chemical Company (Dow) sought methods to directly oxidize propylene to PO to minimize the numerous secondary steps and by-products of the traditional methods. Their initial research indicated that new catalyst systems that promoted silver catalysts could selectively oxidize propylene into PO. Their continued research indicated that catalysts consisting of silver and/or similar elements (for example, gold, titanium, or silica) as catalysts could use hydrogen with oxygen to oxidize propylene directly to PO. Catalysts are used to accelerate the transformation of one chemical to a technologically useful material, for example, in transforming a gas such as ethylene into a plastic such as polyethylene. In 1995, advances in techniques for preparing and activating catalysts led Dow to request funding from ATP in order to develop these processes, which would require less energy and would result in nontoxic carbon dioxide (CO_2) and water (H_2O) as the by-products. The company was unable to raise sufficient internal funds due to the cross-disciplinary nature of the work. Outside academic specialists would assist Dow with specific project tasks. For example, Washington University researchers would conduct analytical studies of catalysts using fast reaction probing of the catalyst as well as using spectroscopy (measuring properties of molecules by probing them with different wavelengths of light). At the National Synchrotron Light Source (NSLS) user facility at Brookhaven National Laboratory in Upton, NY, Dow researchers would analyze reactions using innovative high-resolution synchrotron X-ray methods (using high-frequency electric fields and low-frequency magnetic fields). Researchers at the University of Michigan and Texas A&M University would conduct surface studies of the reactants and the catalysts.

ATP awarded funding for a three-year project, which began in 1995, as part of a focused program, "Catalysis & Biocatalysis Technologies." The ATP support allowed Dow to bring together researchers from the five organizations in a collaborative effort to study the PO reaction over various catalysts. Because direct oxidation is difficult to control, the project was considered very high-risk. Researchers needed to develop a catalyst with a long lifetime and avoid sintering the catalyst (particles sticking together forming larger particles). The oxidation must be selective, producing only PO when the propylene reacts, not other oxidation products such as propanal or acetone, and not other hydrogenation products such as propane and water. The team would study catalysts that included combinations of silver, magnesium, titanium, and gold. To compete with existing chlorohydrin-produced PO, a single-pass conversion rate of at least five percent was necessary (conversion rate is the amount of PO produced divided by the amount of propylene used). The challenge was to obtain acceptable conversion levels that produce only PO and leave the remaining propylene unreacted, so that it can be "cleanly oxidized" on the next pass.

In order to develop a one-step PO process using catalysis, Dow researchers had two primary objectives:

- Understand the ways in which oxidation catalysts work in order to gain higher production efficiency
- Synthesize the catalyst that meets performance goals

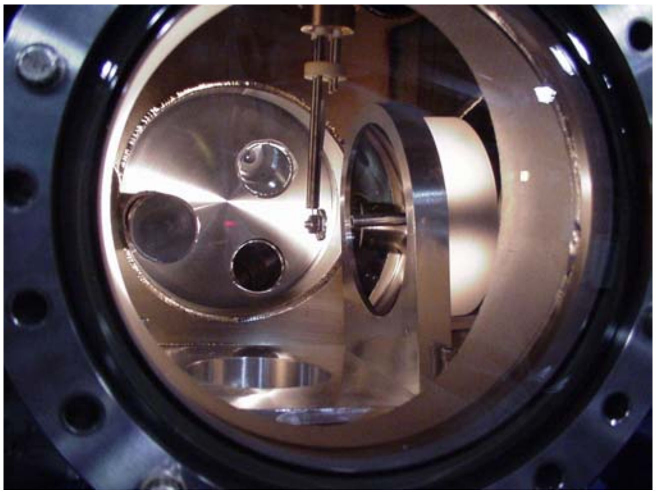
Steps to meet these objectives included the following: (1) identify and synthesize an appropriate catalyst; (2) provide a reaction environment that controls reaction heat and allows rapid diffusion of reactants; (3) achieve long catalyst lifetimes; (4) scale up catalyst production; and (5) engineer the direct oxidation process.

ATP Project Looks inside Chemical Reactions

Selecting the best catalysts was traditionally done by measuring the chemicals produced at the end of a trial. Adjustments and refinements to these trials are based on educated hypotheses. However, the ATP-funded researchers developed a new method to reveal the complex transformations that occur during a chemical reaction (virtually witnessing the reaction happen at various stages of the reaction). Understanding catalysis at a molecular level is vital in order to modify and develop more efficient catalysts.

The challenge was to obtain acceptable conversion levels that produce only propylene oxide and leave the remaining propylene unreacted, so that it can be "cleanly oxidized" on the next pass.

In order to observe chemical reaction intermediates, Dow researchers at the NSLS user facility placed the catalyst (silver, magnesium, gold, titanium, or a combination) in powder-like form in the vacuum-sealed chamber of a soft X-ray detection instrument (Near Edge X-ray Absorption Fine Structure [NEXAFS], see soft X-ray instrument photo). They then sealed the chamber, established a vacuum on the sample, and directed the various reactant gases (oxygen and propylene gas) into the chamber at the catalyst. The catalyst opened the double bond of the propylene molecules and allowed them to oxidize, creating PO. The soft X-ray instrument had never been used in this way before. Intense X-rays were directed at the chamber that contained the reactants and the catalyst. By tuning the wavelength or "color" of the X-rays, the scientists could select low-energy X-rays that probed the reaction intermediates in every step of the reaction. Thus, they could "follow" the reaction's progress, in real time, by observing the changes in the reaction intermediate's "spectral fingerprints" on a computer screen.



The Dow/Brookhaven soft X-ray detection instrument consists of the sample stud (hanging, center, 1-cm diameter), soft X-ray detector (left, tube, 2-cm diameter), and the focusing multilayer mirror (MLM) (right, spherical mirror, 10-cm diameter). Researchers place a small amount of the powder-like catalyst on the sample stud. They close the door, establish a vacuum, and allow oxygen and propylene gas to enter the chamber. The catalyst stimulates a chemical reaction between the propylene (composed of carbon and hydrogen) and oxygen to form PO and nontoxic by-products such as H_2O and CO_2. The X-ray detector takes measurements, and the MLM screens out background spectral images.

The project scientists developed a mirror, called a normal incidence focusing multilayer mirror (MLM) to focus on particular reaction intermediates. The MLM reduced background spectral images and allowed researchers to understand how the reactants and catalysts work together under real conditions at the molecular level. Image resolution was smaller than 300 nanometers (billionths of a meter).

Dow researchers could alter PO output by making changes in temperature, proportions, and additives. They intended to use these measurement results to develop more efficient catalysts for propylene oxidation.

Catalysis Research Makes Progress

During the project, researchers discovered that adding hydrogen (H_2) as an additive with the reactant gases increased the amount of propylene that converts to PO. Furthermore, by the end of the ATP-funded project, Dow researchers were able to control the size and dispersion of catalysts and to identify effective additives, resulting in an even higher yield of propylene to PO. The main by-products were nontoxic CO_2 and H_2O, which would eliminate the industry's concerns about waste disposal. Researchers gained an understanding of the catalysts and developed new methods for studying the synthesis and optimization of catalysts. They worked with catalyst manufacturers to scale up production of identified catalyst compositions.

The multilayer mirror reduced background spectral images and allowed researchers to understand how the reactants and catalysts work together under real conditions at the molecular level.

Dow received six patents for their innovations, with three more patents pending. Researchers on the ATP-funded project disseminated their results widely in academic publications and through presentations. However, unexpected volatility in the price of hydrogen has been a barrier to commercialization. Some of the hydrogen additive is wasted, because instead of converting propylene to PO, it converts some propylene to propane and some of the oxygen to water. Also, researchers are still trying to develop a cost-effective catalyst with a long lifetime. Dow continues to fund this PO direct-oxidation research to achieve higher conversion rates and lifetimes. Researchers believe they may complete a process sometime between 2006 and 2014. Single-step direct oxidation is the ultimate objective of PO, so all the global competitors, such as Sumitomo, Lyondell, Degussa/Krupp Uhde, and BASF, are working to develop this technology.

Dow researchers are also using direct-oxidation techniques from this project to design new catalysts to pursue other industrially important chemicals (such as butylene oxide). They hope to develop new production methods for polymers, metal-polymer interfaces, solvents, and lubricants, as well as stronger coatings and adhesives.

Manufacturers Keep Their Production Options Open

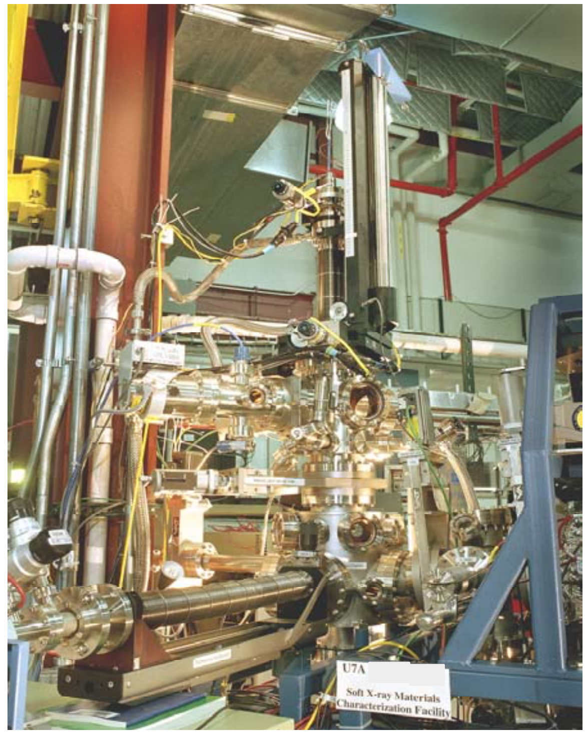
PO production is an important business for The Dow Chemical Company, so the company invests in multiple manufacturing methods simultaneously. For example, the company acquired an exclusive license from a Russian firm, JSC Nizhnekamskneftekhim, to use an organic hydroperoxide-based PO manufacturing process, as reported in *Chemical Engineering*. Dow and BASF also formalized an agreement to develop and commercialize the hydrogen peroxide process for PO in 2002. The main drawback of this process is its large consumption of hydrogen peroxide, which would entail incorporating a new adjacent hydrogen peroxide plant. Dow planned to use this method in a plant on the U.S. Gulf Coast in 2004; however, this project has been delayed because Dow lowered its PO demand forecast in response to the economic downturn in North America in 2001. In commodity markets, such as PO, manufacturers compete for fractions of pennies per pound of PO. Margins are small and slight cost variations can make production methods untenable.

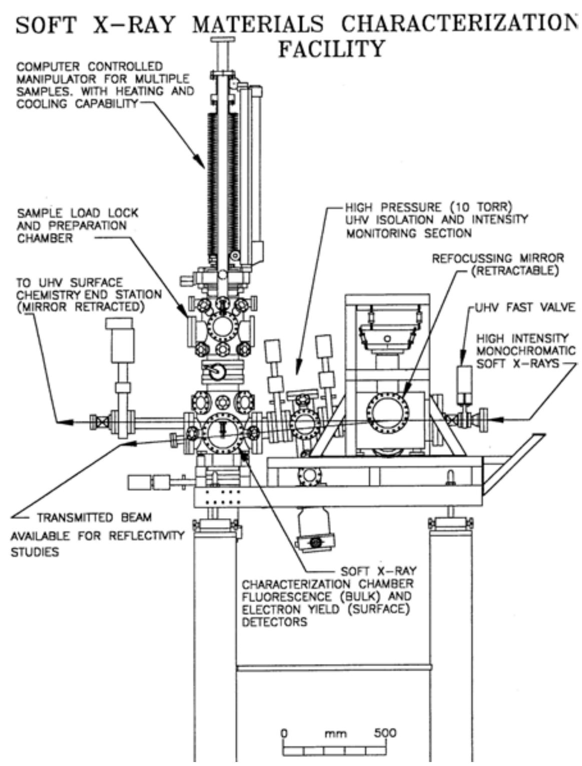
The scientists could "follow" the reaction's progress, in real time, on a computer screen.

Dow and its competitors continue to pursue direct oxidation methods and alternative technologies. As of 2004, the chlorohydrin and hydroperoxide processes still dominate the global market. Direct oxidation of PO could be the easiest method, if the conversion rate can be raised high enough to achieve cost competitiveness. Dow believes that, depending on the site and availability of raw materials, any of these various technologies could become cost effective, so the company continues to explore all of the PO processes. Developing direct-oxidation PO methods remains a priority for Dow.

New In Situ Catalyst Characterization Technique Leads to Spillover Applications

Dow worked as a member of the beamline user facility located at U7A of the NSLS at the Brookhaven National Laboratory. They were able to characterize leading edge materials and improve their understanding of how to control oxidative catalysis. Collaborations at this facility advanced in situ catalyst characterization using soft X-ray detection technology (NEXAFS) and led to more industrial users exploring the potential of this in situ tool for catalyst characterization long after the ATP award.





Photograph and diagram of the soft X-ray instruments. The sample is placed in a chamber at about midpoint in the tower at the center of the photograph. The soft X-ray beams enter from the right.

From 1998-2000, following the ATP project, several companies collaborated with NIST researchers to perform additional non-proprietary catalysis characterization research at the NSLS at Brookhaven National Laboratory. The collaborating companies included Texaco, Intevac, UOP, and Rohm & Haas. They continued to enhance the NEXAFS soft X-ray detection technology , automating it and making it more user friendly, and used the multilayer mirror developed in this ATP-funded project. Some examples of discoveries include the following: the ability to manipulate particles on a nanoscale (creating a patterned assembly of gold nanoparticles for specialized filters, sensors, high-efficiency solar cells, single-molecule detectors, and in the future potentially to be used for high-density information storage devices); adjust surface chemistry of biomaterials to optimize artificial polymer joints to last longer; and the electronic structure of superconductors in order to improve performance. Soft X-ray spectroscopy has also provided critical insight on performance-limiting chemistry challenges for next-generation nanometer-scale structures in integrated circuits and showed that lubricant additives were chemically interacting with the protective overcoat needed in future high-capacity computer hard disks.

The soft X-ray work broadly benefits catalysis technology by improving scientists' understanding of what makes a good catalyst under "industrial" operating conditions and has led to numerous publications. In 2004, a key NIST researcher doing research at the Brookhaven NSLS, Dr. Daniel Fischer, was awarded a Department of Commerce Gold Medal for Scientific/Engineering Achievement for his work on "a unique national measurement facility for soft X-ray absorption spectroscopy enabling breakthrough materials advances."

Conclusion

During this ATP-funded research, The Dow Chemical Company and its subcontractors made significant progress in analyzing and understanding direct-oxidation reactions to produce propylene oxide (PO), as well as developing methodologies that will affect using direct oxidation catalysis in new ways for other products. If successful, improved PO production will positively affect a huge volume and diversity of products, such as polyurethane-foams (inside upholstery), adhesives, coatings, sealants, pharmaceuticals, cosmetics, packaging, antifreeze, soaps, solvents, and lubricants. Despite Dow's substantial additional research, the direct oxidation process for PO is not yet economically feasible due to the fluctuating cost of hydrogen. The company believes that it might successfully complete a direct-oxidation process for PO in the future (2006–2014) that will be faster and less expensive and will result in nontoxic by-products (carbon dioxide and water). Although still technically risky, if successful, direct-oxidation processes could be applied to other petrochemical gases such as butene. New conversion methods could lead to producing PO and other petrochemical derivatives with little waste and lower energy consumption.

PROJECT HIGHLIGHTS
The Dow Chemical Company

Project Title: Using Catalysts to Directly Oxidize Propylene to Propylene Oxide (Breakthrough Process for Direct Oxidation of Propylene to Propylene Oxide)

Project: To develop a direct, economical, single-step oxidation process that incorporates a silver-based catalyst to convert propylene to propylene oxide (PO).

Duration: 10/1/1995–9/30/1998
ATP Number: 95-05-0002

Funding(in thousands):**

ATP Final Cost	$1,958	71%
Participant Final Cost	802	29%
Total	$2,760	

Accomplishments: With ATP funding, The Dow Chemical Company and its subcontractors improved PO oxidation efficiency and stimulated substantial ongoing research. Researchers gained a better understanding of catalysts and made advances in their ability to observe chemical reactions in "real-time" using a soft X-ray detection instrument. Project researchers also developed a new tool that they added to the soft X-ray instrument called a focusing multilayer mirror, which filters out background spectral images.

Following the ATP-funded project, researchers from several companies and NIST continued to collaborate on non-proprietary catalyst research and development using the tools and methods of this ATP-funded project. Collaborating companies included Dow, Texaco, Intevac, UOP, and Rohm & Hass, from 1998-2000. The ongoing development resulted in numerous publications and one technical award:

- Gold Medal for Scientific/Engineering Achievement for Dr. Daniel Fischer's work on "a unique national measurement facility for soft X-ray absorption spectroscopy enabling breakthrough materials advances." Awarded by the Department of Commerce, NIST/Brookhaven National Laboratory, 2004.

Dow has received six patents for oxidation technologies developed during this ATP-funded project. Three additional patent applications are pending.

- "Process for the direct oxidation of olefins to olefin oxides"
(No. 5,965,754: filed December 11, 1998; granted October 12, 1999)
- "Process for the direct oxidation of olefins to olefin oxides"
(No. 6,646,142: filed December 7, 1999; granted November 11, 2003)
- "Process for the direct oxidation of olefins to olefin oxides"
(No. 6,323,351: filed December 9, 1999; granted November 27, 2001)
- "Process for the direct oxidation of olefins to olefin oxides"
(No. 6,362,349: filed October 4, 2000; granted March 26, 2002)
- "Process for the direct oxidation of olefins to olefin oxides"
(No. 6,562,986: filed February 19, 2002; granted May 13, 2003)
- "Process for the direct oxidation of olefins to olefin oxides"
(No. 6,670,491: filed January 14, 2003; granted December 30, 2003)

Commercialization Status: Direct oxidation of propylene to PO is still Dow's ultimate goal. Dow researchers expect that they might complete a process sometime between 2006 and 2014. A successful process will reduce energy consumption, cost, and waste in the manufacturing of many types of plastics, lubricants, coatings, surfactants (detergents), and composite materials.

Outlook: The outlook for the direct oxidation of propylene is good, but still technically risky. If Dow can overcome the technical barriers and finalize the direct-oxidation process before its competitors are able to bring a new process to market, the company will be in a strong position to compete in the global PO market.

Composite Performance Score: * * *

Focused Program: Catalysis & Biocatalysis Technologies, 1995

** As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs. Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.

PROJECT HIGHLIGHTS
The Dow Chemical Company

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  College Station, TX
- Washington University
  Chemical Engineering Department
  St. Louis, MO
- University of Michiga
  College of Engineering
  Ann Arbor, MI
- Brookhaven National Laboratory (National Synchrotron Light Source [NSLS] user facility)
  Upton, NY

Publications: Researchers disseminated their knowledge widely through 37 academic publications.

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- "Soft X-ray Absorption Spectroscopy for In Situ Catalyst Characterization." Plenary Speaker, 14th International Congress on Catalysis, Baltimore, MD, June 29, 1996.

- "Soft X-Ray Materials Characterization Facility: Catalysis Applications." Catalysis, Biocatalysis, and Separations Technology Advanced Technology Program Review, Boulder, CO, October 22, 1996.

- "The Application of Solid State Detectors in Ultra Soft X-ray Absorption Spectroscopy." International Radiation Detectors, Torrance, CA, January 15, 1997.

- "Soft X-Ray Surface Chemistry Characterization: Tribochemical and Thermochemical Reactions of Stearic Acid on Metal Surfaces." National Storage and Information Consortium Meeting, San Diego, CA, January 16, 1997.

- "Chemistry and orientation of lubricants on hard disk magnetic media substrates: characterization by NEXAFS." National Storage and Information Consortium Meeting, Berkeley, CA, January 23, 1998.

- "Dow/NIST materials characterization facility: catalysis applications." Advanced Technology Program, Catalysis and Separations Technologies Program Workshop, February 18, 1998.

- “XANES Research at the Dow/NIST Soft X-ray Materials Characterization Facility” NSLS Users Annual Meeting, May 20, 1998.

- "Synchrotron Based Low Z Materials Analysis." American Vacuum Society International Symposium, Baltimore, MD, November 2, 1998.

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- "Focusing Wavelength Dispersive Multilayer Detection System for Soft X-ray Absorption Spectroscopy." NSLS Users Meeting, May 24, 1999.

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